Solid phase extraction method for the study of black carbon cycling in dissolved organic carbon using radiocarbon

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Abstract: Radiocarbon analysis is a powerful tool for understanding the cycling of individual components within carbon pools, such as black carbon (BC) in dissolved organic carbon (DOC). Radiocarbon (Δ14C) measurements of BC in DOC provide insight into one source of aged, recalcitrant DOC. We report a modified solid phase extraction (SPE) method to concentrate 43 ± 6% of DOC (SPE-DOC) from seawater. We used the Benzene Polycarboxylic Acid (BPCA) method to isolate BC from SPE-DOC (SPE-BC) for subsequent 14C analysis. We report SPE-BC Δ14C values, SPE-BC concentrations, and the relative BPCA distributions from Milli-Q water process blanks, two riverine reference standards, as well as a coastal and an open ocean surface water sample. The composition of BC is less aromatic in the ocean samples than those in the river standards. We find higher BC Δ14C values in the river standards (+ 148 to − 462‰) than BC in the ocean samples (− 592 to − 712‰), suggesting that BC ages within oceanic DOC. We report that BC is 4.2 ± 1.0% of SPE-DOC in the open ocean surface sample, or 1.4 ± 0.1 M C. This work provides the methodological basis by which global BC concentrations, compositions (e.g. relative abundances of BPCA marker compounds) and Δ14C values can be assessed.

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Solid phase extraction method for quantification and compound-specific radiocarbon analysis of black carbon in dissolved organic carbon

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Abstract:

Compound specific radiocarbon analysis (CSRA) is a powerful tool for understanding the cycling of individual components within total carbon pools, such as black carbon (BC) within dissolved organic carbon (DOC). Radiocarbon ($\Delta^{14}C$) measurements of BC provide insight into one source of aged, recalcitrant DOC. We have developed a solid phase extraction (SPE) method that uses a wide polarity range of solvents to concentrate 43±6% of DOC from seawater and 62±5% from freshwater. We use the Benzene Polycarboxylic Acid (BPCA) method to isolate BC from polar to non-polar SPE-DOC for subsequent CSRA. We report SPE-BC $\Delta^{14}C$ values, BC concentrations, and the relative BPCA distributions from Milli-Q water process blanks, two riverine reference standards, and coastal and open ocean surface samples. The composition of BC is less aromatic in the ocean samples than those in the river standards. We find higher BC $\Delta^{14}C$ values in the river standards (+148 to -462‰) than BC in the ocean samples (-592 to -712‰), suggesting that BC ages within oceanic DOC. We report that BC is 5±2% of SPE-DOC in the open ocean surface sample, or 1.5±0.6 μM C. This work provides the methodological basis for which global BC concentrations, compositions (eg. relative abundances of BPCA marker compounds) and $\Delta^{14}C$ values can be assessed.

Keywords: solid phase extraction, dissolved organic carbon, BC, radiocarbon, BPCA, recalcitrant RDOC, Station M, Compound specific radiocarbon analysis, preparative capillary gas chromatography, Suwannee River

1. Introduction

Black carbon (BC) is formed from incomplete combustion of fossil fuels and biomass. BC plays a strong role in the climate system, as it is considered second to CO_2 as the most important human emission based on its forcing (Bond et al., 2013; Husain et al., 2007; Novakov and Rosen, 2013). BC also is hypothesized to be a long term carbon sink (Masiello and Druffel, 1998; Dai et al., 2005; Kuhlbusch and Crutzen, 1995), as it's structure is composed of condensed aromatic rings making it stable and resistant to biological degradation (Goldberg, 1985; Forbes et al., 2006). After a fire, large amounts of charcoal in soils are oxidized and transported to riversheds (Kim et al., 2004; Hockaday et al., 2007; Mannino and Harvey, 2004; Preston and Schmidt, 2006). BC is transported to the ocean by rivers, and is ubiquitous in the water column and sediments (Jaffe et al., 2013; Dittmar and Paeng, 2009; Stubbins et al., 2012; Ziolkowski and Druffel, 2010; Suman et al., 1997; Masiello and Druffel, 1998; Coppola et al., 2014).

Once BC enters the ocean, it contributes to one of Earth's major organic carbon reservoirs, dissolved organic carbon (DOC, <0.2 μm). While most DOC is produced by phytoplankton in the surface ocean, marine DOC is surprisingly thousands of years old (Williams and Druffel, 1987). The presence of recalcitrant BC within the marine DOC pool may explain this mystery, as DOC may act as a "holding pool" for BC (Ziolkowski and Druffel, 2010; Masiello and Druffel, 1998). Two studies have identified BC in solid phase extracted DOC (SPE-DOC) with concentrations ranging from 0.6 to 0.8 μM (1 to 2% of total DOC) in the Southern Ocean (Dittmar and Paeng, 2009) and 1.0 ±0.2 μM BC in surface North Atlantic Deep Water at the Bermuda Atlantic Time Series site (Stubbins et al., 2012). Ziolkowski and Druffel (2010) made the only BC $\Delta^{14}C$ measurements in the DOC pool using ultrafiltered DOC (UDOC). They found open ocean BC had a range of ages from 15,680 to 20,100 ^{14}C yrs in UDOC,

providing evidence for BC stability on millennial time scales. Corresponding BC in UDOC ranged from 0.09 μM to 0.33 μM C in the North Central Pacific (NCP) and Northeast Pacific open ocean.

BC $\Delta^{14}C$ measurements in UDOC have limitations for evaluating the entire DOC pool, because UDOC is only ~25% of DOC and primarily collects high molecular weight compounds (>1000 Da) (Amon and Benner, 1996; Walker et al., 2011; Benner, 2002; Aluwihare et al., 2002; Repeta et al., 2002; Benner et al., 1997). Studies of chemical composition and ^{14}C age of marine organic carbon show that the age and complexity of organic carbon increases with smaller sized molecules (Benner and Amon, 2015; Santschi et al., 1995; Walker et al., 2011). Thus, the presumably oldest, low molecular weight BC is not captured in UDOC. We measured BC $\Delta^{14}C$ in a larger fraction of the DOC pool using SPE, without an inherent size bias. The SPE method concentrates DOC based on chemical composition, retaining polar and non-polar DOC compounds. This BC extraction method for Compound Specific Radiocarbon Analysis (CSRA) is an improvement over UDOC, because SPE recovers approximately half of the total DOC pool (Dittmar, 2008), without the time required for laborious UDOC isolations.

We use a styrene divinyl benzene copolymer (HP-20, 200 Å pore size) resin to concentrate DOC. Most of the DOC we isolate is hydrophilic; we use additional non-polar solvents to elute the hydrophobic DOC fraction that is adsorbed on the resin bed. We measure the mass and $\Delta^{14}C$ value of SPE-DOC from Milli-Q water, two riverine reference standards, and marine samples from a coastal and an open ocean site off California. We assess blanks, reproducibility and the robustness of this SPE-DOC method. Comparisons of SPE-DOC to total UV-oxidized DOC are used to evaluate whether SPE-DOC $\Delta^{14}C$ values are representative of total DOC $\Delta^{14}C$.

93 We then isolate BC from the SPE-DOC samples (SPE-BC) using the Benzene
94 Polycarboxylic Acid (BPCA) method, which oxidizes BC into marker compounds (BPCAs) for
95 CSRA. The relative abundances of BPCAs produced during the oxidation step also provide
96 qualitative BC structural information, because the more substituted BPCAs are derived from a
97 more condensed aromatic BC network (Glaser et al. 1998; Ziolkowski et al., 2011; Coppola et al.,
98 2013). The structural composition and $\Delta^{14}C$ values of SPE-BC provides insight into the
99 composition of recalcitrant DOC, which escapes decomposition for thousands of years (Hansell
100 et al., 2012; Ziolkowski and Druffel 2010; Jiao et al. 2010; Stubbins et al., 2012). Our primary
101 motivation is to use this SPE method to investigate aged BC contributions to recalcitrant DOC
102 by determining the distribution and ^{14}C age of BC in the ocean.
103
104 **2. Materials and Methods:**
105 *2.1. Sample Collection*
106 Coastal seawater DOC samples were collected from Newport Beach Pier (NBP)
107 ($33^{o}60.70$'N, $117^{o}92.89$'W) on August 8, 2013 at 1 m depth in 1-gallon jugs. Open ocean
108 seawater DOC samples were collected from 20 m depth at Station M located on the Pacific
109 abyssal plain (34°50'N, 123°00'W) on the *R/V* New Horizon in November 2004 using Niskin
110 bottles. NBP samples were filtered through 1.0 μm Whatman filters and Station M DOC
111 samples were filtered using Whatman Polycap AS filter capsules (0.2 μm). All glassware in this
112 study was soaked in 10% HCl, rinsed with deonized water and combusted at $550^{o}C$ for 2 hrs. All
113 seawater samples were frozen (at -20°C) until analysis. Seawater samples were separately
114 analyzed for total DOC $\Delta^{14}C$ and [DOC] values using UV-oxidation techniques (Beaupré et al.,
115 2007).

Seawater samples collected from Station M are from a long-term abyssal study site (4100m), located ~220 km west of Point Conception, CA in the NE Pacific (Smith and Druffel, 1998). The California current flows southward at Station M and has well-developed spring blooms. NBP is a coastal site, impacted by urban river discharge from the nearby Santa Ana River (5km north of NBP) during rain events in southern California. There was no river events recorded by the rain gauge on the Santa Ana River in the City of Santa Ana on August 8, 2013 (available on the USGS site, see Supplementary Figure 1).

2.2. Suwannee River Natural Organic Matter Standards

We used two freshwater, organic matter reference samples from the International Humics Substances Society (https://ihss.humicsubstances.org/) collected in 1999 and 2012. The Suwannee River drains the Okefenokee Swamp in southeastern Georgia, located at 30°48'14'N, 82°25'03'W and has high DOC concentrations (82.7 mg/L) with low concentrations of inorganic solutes (Serkiz and Perdue, 1990; Green et al., 2015). To create these standard, large volumes of water (~36,000L) from the Suwannee River were concentrated by reverse osmosis, desalted by cation exchange, freeze-dried and homogenized.

We used two Suwannee River Natural Organic Matter standards collected using the same methodology at different times. Suwannee River I (IHSS 1R101N termed SR NOM I) was collected from May 1-9, 1999. Suwannee River Natural Organic Matter II (IHSS2R101N termed SR NOM II) was collected from May 3-15, 2012 (Green et al., 2012). When SR NOM I was sampled, two dams (built in 1950-1960) in the Suwannee River sill retained a high water level in the swamp and the site was relatively pristine and vehicle access was prohibited (Green et al., 2015). The average flow rate of the river was 1.96 m^3/s. In 2012, one of the two dams had been

139 removed and it was no longer pristine (Green et al., 2015). The water level during 2012 was
140 lower and the flow rate much lower than in 1999 (0.46 m^3/s). Both SR NOM I and SR NOM II
141 were dissolved in Milli-Q water at DOC concentrations of 75–85 μM for BC analysis.
142
143 *2.3. Solid Phase Extraction of DOC (SPE-DOC)*
144 We used a styrene divinyl benzene copolymer sorbent (Sigma Aldrich Diaion 13605, HP-
145 20, pore size 200 Å), first used by De Jesus and Aluwihare (2008). To minimize the resin carbon
146 blank, extensive cleaning (~1 week) was performed using a glass soxhlet extractor with a pyrex
147 glass insert to hold the resin during washings of methanol, acetone, ethyl acetate and
148 dicholormethane at 65°C, 56°C, 77°C and 40°C, respectively. Each soxlet solvent washing lasted
149 24 hours and was performed sequentially in order of decreasing polarity. According to the HP-20
150 manufacturers guidelines, sample water was acidified to pH 2 with hydrochloric acid (Fluka
151 Traceselect 84415-500 ml) to increase extraction efficiency.
152 Figure 1 summarizes the SPE and BC methods. Briefly, large-volume water samples (10
153 – 15 L) were defrosted, homogenized by shaking and loaded onto the column. Samples were
154 siphoned through 15 ml of resin in a glass Kontes column using 6 mm diameter pyrex tubing
155 with acid cleaned silicone tubing at a slow loading rate of 16 bed volumes per hour (240 ml/hr
156 for surface samples). This flow rate was monitored and maintained over the course of the
157 sample loading. The sample was loaded onto the resin three times to maximize interaction of
158 DOC with the resin bed and increase DOC recovery.
159 In preparation for DOC elution, two bed volumes (30 ml) of Milli-Q water were passed
160 through the column at 30 ml/hr to remove salts, and this fraction was discarded. SPE-DOC was
161 eluted with solvents, each at a flow rate of 30 ml/hr using two bed volumes (30 ml). Solvents

with different polarities were used to elute SPE-DOC into pre-combusted glass vials in the following order: methanol, acetone, ethyl acetate and dicholoromethane. These SPE-DOC fractions were dried under a stream of ultra-high purity nitrogen gas. The SPE-DOC fractions were dissolved in a known volume of solvent, sub-sampled (5-10% of the volume), dried under ultra-high purity nitrogen, then lyophilized for 24 hours. The SPE-DOC fractions were combusted separately to determine the percent yield of DOC (SPE-DOC/total DOC x 100) and for comparisons of SPE-DOC Δ^{14}Cand total DOC Δ^{14}C analyses.

2.4. BC in Solid Phase Extracted DOC (SPE-BC)

The SPE-DOC methanol fractions were used to isolate BC using the BPCA method (Ziolkowski et al., 2011; Schneider et al., 2011). Briefly, eluted SPE-DOC extracts were dried and lyophilized for 24 hrs. Concentrated nitric acid was added and placed in a quartz pressure digestion chamber at 170°C for 8 hours to produce BPCAs (Coppola et al., 2013; Ziolkowski et al., 2011). The carbon in the carboxylic acid groups of the BPCA compounds is derived from adjacent aromatic groups of BC (B3CA, substituted with three carboxylic acids through B6CAs, those substituted with six carboxylic acids). After digestion, the solution was filtered, lyophilized and re-dissolved in methanol. Samples were derivatized using (trimethylsily) diazomethane in 2.0 M diethyl ether to convert carboxylic acid groups to methyl esters and an internal standard was added (500 µml of 2-2', biphenol). BPCAs were collected on the preparative capillary gas chromatograph (PCGC), along with other BC standards (Hammes et al., 2007; Wiedemeier et al., 2015) using previously published techniques (Ziolkowski and Druffel, 2009; Coppola et al., 2013). In preparation for CSRA analysis, B3CA through B6CA marker compounds (including nitrated B3CA and B4CAs) were collected in U-traps (-20°C) in the fraction collector. The

185 B2CA marker compounds were not collected, because they may derive from lignins. The
186 BPCAs in the U-trap were transferred using dichloromethane to clean quartz tubes, and dried
187 under UHP nitrogen.
188
189 *2.5. Radiocarbon Analyses*
190 For $\Delta^{14}C$ analysis, samples were sealed in quartz tubes under vacuum with cupric oxide
191 and silver wire and combusted to CO_2 at 850°C for 2 hrs. The CO_2 gas produced was
192 cryogenically purified, and quantified manometrically. The manometric determinations of SPE-
193 DOC combusted subsamples were used to calculate % DOC recovery. In some cases when
194 sample sizes were too small for individual $\Delta^{14}C$ measurement (e.g., ethyl acetate and
195 dichloromethane) fractions were combined and so-labeled. For all samples, CO_2 was reduced to
196 graphite for $\Delta^{14}C$ analysis using a sealed tube zinc reduction method (Xu et al. 2007; Khosh et al.,
197 2010). Radiocarbon measurements were made at the UCI Keck Carbon Cycle Accelerator Mass
198 Spectrometry Laboratory and are reported as $\Delta^{14}C$ for geochemical samples without known age
199 correction (Stuiver and Polach, 1977).
200
201 *2.6. Carbon Blanks: Resin Blank and Process Blank Assessments*
202 Resin blanks were processed to assess the carbon blank from each solvent that was
203 passed through the resin before loading a sample. Resin blanks ranged from 2 to 6 μg C.
204 Process blanks contained Milli-Q water (10 L each) and were subjected to the same preparatory
205 steps as the samples. Process blanks were used to correct samples for the $\Delta^{14}C$ value and mass
206 of carbon blank added during processing, using a mass balance approach in Equation 1:
207 $$\Delta^{14}C_{SPE-DOC} = \frac{\Delta^{14}C_{measured}C_{measured} - \Delta^{14}C_{Milli-Q}C_{Milli-Q}}{C_{measured} - C_{Milli-Q}} \quad \text{(Equation 1)}$$

where $\Delta^{14}C_{SPE-DOC}$ is the radiocarbon value corrected for SPE processing, $\Delta^{14}C_{measured}$ and $C_{measured}$ are the measured Δ^{14}C value and mass of the sample uncorrected for SPE processing, $\Delta^{14}C_{Milli-Q}$ and $C_{Milli-Q}$ are the average Δ^{14}C value and mass of the Milli-Q water SPE-DOC, respectively (Table 1).

For the assessment of blank carbon during the BPCA method, process blanks were generated using Milli-Q water. The SPE-BC samples are corrected using an indirect approach as previously by reported Coppola et al., (2013) and Ziolkowski and Druffel (2009). Several dead (-1000‰) and modern BC standards from Hammes et al., (2007) were run alongside SPE-BC samples to correct for blank carbon. Approximately 6 to 10 μg C dead blank C and 0.5 μg C of modern carbon was added during BC processing.

3. Results

3.1. Carbon Blank assessments

The mass of resin blanks from each of the four solvents range from 2 to 8 μg C, and their Δ^{14}C values range from -499±14‰ to -873±2‰ (Supplementary Table 1). The Δ^{14}C values of Milli-Q process blanks range from -660‰ to -1000‰, and had masses that range from 2 to 10 μg C (Table 1). Using an isotopic mass balance, we determine Milli-Q water SPE-DOC Δ^{14}C values range between -721±77‰ to -927±54‰ (Supplementary Table 1). The Milli-Q water total DOC Δ^{14}C values obtained using UV-oxidation techniques range from -612±57 to -926±57‰, which is equal to the range in SPE-DOC Milli-Q Δ^{14}C values.

3.2. SPE-DOC recoveries and $\Delta^{14}C$ values

231 Percent SPE-DOC recoveries in all elutants for SR NOM I, SR NOM II, NBP and Station
232 M samples are 62±5%, 61±4%, 43±6% and 44±3%, respectively (Figure 2, Table 2). Percent
233 SPE-DOC recoveries for ocean samples are comparable to those reported by Dittmar (2008)
234 (42±8%) for surface marine DOC using a similar method (pre-made PPL cartridges with a
235 smaller pore size of 150 Å and methanol elution).
236 For all samples, most of the DOC (>89%) was eluted in the methanol fraction (Table 2,
237 Figure 3). Suwannee River NOM I and II standards had a very small amount of DOC (~1%) that
238 eluted in the acetone fraction, and no DOC eluted in the ethyl acetate and dichloromethane
239 fractions. For NBP, although the majority (92±4%) of coastal SPE-DOC was present in the
240 methanol fraction, the non-polar fractions constitute 8% of the SPE-DOC (acetone 4±2%, ethyl
241 acetate 2±1% and dichloromethane 2±1%). At Station M, the methanol fraction is 89±2%,
242 dichloromethane is 9±2% and there were insignificant DOC in the acetone and ethyl acetate
243 fractions (1±1%) for BC measurements.
244 The methanol SPE-DOC $\Delta^{14}C$ values for SR NOM I are identical within 1 sigma
245 (+110±7‰, +105±10‰, +114±8‰)(Figure 2). The acetone SPE-DOC fractions in SR NOM I
246 are -286±81‰ and -124±68‰, significantly lower than those of the methanol fractions. The
247 $\Delta^{14}C$ value of total combusted SR NOM I is +152±3‰ (Table 2), which is significantly higher
248 than that of the methanol fractions, indicating that the SPE-DOC fraction is selectively isolating
249 older DOC from the bulk material.
250 Duplicate methanol SPE-DOC $\Delta^{14}C$ values in SR NOM II are identical (+20±16‰,
251 +20±18‰)(Figure 2b). The acetone fraction $\Delta^{14}C$ values (-329±57‰ and -480±75‰) are
252 significantly lower than the methanol fractions. The total combusted SR NOM II $\Delta^{14}C$ value

253 (+45±3‰) is within 2 sigma of the SPE-DOC $\Delta^{14}C$ values measured in the methanol fractions
254 (Table 2).
255 Duplicate methanol SPE-DOC $\Delta^{14}C$ values in NBP seawater are identical (-263±10‰,
256 -255±12‰) (Figure 2). The acetone SPE-DOC $\Delta^{14}C$ values are -717±24‰ and -764±10‰,
257 which were much lower than those of the methanol fractions. The $\Delta^{14}C$ values of the ethyl
258 acetate/dichloromethane combined fractions are intermediate or equal to the two other fractions
259 (-543±41‰ to -691±95‰ Table 2). The NBP total DOC $\Delta^{14}C$ values measured by UV-oxidation
260 are -246±3‰, which is also equal to the methanol fraction $\Delta^{14}C$ value.
261 For Station M seawater, the methanol SPE-DOC $\Delta^{14}C$ values are -318±11‰ and
262 -335±7‰(Figure 2). The other fractions have lower $\Delta^{14}C$ values (acetone -678±25‰, ethyl
263 acetate/dichloromethane -958±5‰) (Table 2). The total Station M DOC $\Delta^{14}C$ value is -299±3‰,
264 which was significantly higher than one of the methanol fraction values and equal to the other
265 value.
266
267 *3.3. BC concentration, and relative BPCA distributions*
268 The average BC/OC% values in SR NOM I, SR NOM II, NBP and Station M seawater
269 samples are 10±3%, 11±2%, 20±2% and 5±1%, respectively (Table 3, Supplementary Table 2).
270 The BC concentrations at the NBP and Station M sites are 4±0.4 μM and 1.5±0.6 μM,
271 respectively, in the SPE-DOC (Supplementary Table 2).
272 The relative BPCA abundances (i.e. B3CA, B4CA, B5CA, B6CA) in the methanol
273 fractions of SR NOM I and II have low B3CAs and B4CAs abundances relative to those for
274 B5CAs and B6CAs. However, between SR NOM samples, there is a greater abundance of
275 B6CAs in SR NOM II collected in 2012. In contrast, the NBP samples have similar abundances

276 of B3CAs, B4CAs and B5CAs and a low abundance of B6CAs (7±3%). We obtained BPCA
277 abundances for the less polar SPE-BC fractions for the NBP samples only (Figure 4b), and the
278 only significant difference between methanol with other non-polar fractions is the absence of
279 B6CA marker compounds. The BPCA abundances in the Station M samples (Figure 4a) reveal a
280 greater proportion of B3CAs than at NBP.
281
282 *3.4 SPE-BC $\Delta^{14}C$ values*
283 SPE-BC $\Delta^{14}C$ values for the SR NOM standards, and those for the NBP and Station M
284 seawater samples are listed in Table 3 and shown in Figure 4a. The methanol SPE-BC $\Delta^{14}C$
285 value of SR NOM I are +148±17‰. Total BC $\Delta^{14}C$ for SR NOM I was -49±33‰, which is
286 significantly lower than that for the methanol SPE-BC. In contrast, duplicates for methanol SPE-
287 BC of SR NOM II are -462±40‰ and -346±70‰ (within 2 sigma), however total BC $\Delta^{14}C$ for
288 SR NOM II (-159±55‰) is higher than the methanol $\Delta^{14}C$ SPE-BC value.
289 The methanol SPE-BC $\Delta^{14}C$ values in NBP seawater are -712±36‰ and -678±19‰
290 (within 2 sigma). The SPE-BC $\Delta^{14}C$ values of the acetone fractions are -587±47‰ and -
291 615±20‰. The NBP SPE-BC $\Delta^{14}C$ value of the ethyl acetate/dichloromethane mixture are -
292 593±15‰, which was equal to the acetone fractions of NBP SPE-BC fractions (Figure 4b).
293 The methanol SPE-BC $\Delta^{14}C$ values in the Station M seawater samples are -592±201‰
294 and -649±121‰ (within 2 sigma), equal to the NBP methanol values (Figure 4a). No results
295 were obtained for the acetone, dichloromethane or ethyl acetate fractions.
296
297 **4. Discussion**
298 In the first section of the discussion, we highlight the application of the SPE-DOC
299 method, addressing the reproducibility of concentration and isotopic measurements. We

300 highlight results from standards, blanks and replicate samples. In section 4.2, we discuss the
301 variability of $\Delta^{14}C$ values obtained on the same sample for SPE-DOC and total DOC analysis. In
302 section 4.3, we compare $\Delta^{14}C$ values obtained for SPE-BC and total BC for SR NOM I and II.
303 We also compare our results to those available for from a deep UDOC BC sample in the
304 Northeast Pacific and a surface sample in the North Central Pacific (NCP) (Ziolkowski and
305 Druffel, 2010). In the final section, we discuss SPE-DOC and BC composition and cycling in
306 these aqueous environments.
307
308 4.1 Methods assessment: Recoveries, SPE-DOC carbon blanks and reproducibility
309 Replicate measurements of SPE-DOC and SPE-BC recoveries and $\Delta^{14}C$ values agree
310 within 2 sigma. This demonstrates that use of the method produces reproducible $\Delta^{14}C$ results
311 (Table 2, Table 3, Figure 2). Recoveries are higher for freshwater samples (62±5%), likely due to
312 the absence of salt in the sample. Recoveries were also consistent and reproducible for each
313 sample type (Figure 2).
314 We report that masses of resin blanks acquired prior to sample loading, and Milli-Q
315 process blanks are equal within error (Table 1, Supplementary Table 1), indicating that there is
316 no additional carbon blank introduced to the large volume water samples. The SPE-DOC $\Delta^{14}C$
317 values of Milli-Q process blanks are equal within error to the $\Delta^{14}C$ values obtained for multiple
318 1-L UV oxidized Milli-Q blanks run from 2012-2014 in our laboratory (Supplementary Table 1).
319 The SPE-Milli-Q process blank correction changed $\Delta^{14}C$ values by less than 10‰.
320 The SPE-BC process blanks are similar in size and $\Delta^{14}C$ value to that of resin and Milli-Q
321 process blanks (Table 3). The SPE-BC process blanks are also comparable to those reported by

322 Coppola et al., (2013). Together, these results suggest that no additional carbon blank is
323 introduced by the SPE method and this method has low, consistent carbon blanks.
324
325 4.2 Comparison of SPE-DOC and total DOC $\Delta^{14}C$ values
326 We present the first $\Delta^{14}C$ comparison between SPE-DOC and UV oxidized total DOC
327 from splits from the same sample water (Table 2). Generally, we find that all methanol SPE-
328 DOC $\Delta^{14}C$ values are equal to or lower (~25±10‰) than their corresponding total DOC $\Delta^{14}C$
329 values, presumably because SPE chemically fractionates the DOC (Figure 2). Similarly, SPE-
330 DOC of SR NOM I and II standards are significantly lower (~35±10‰) than total DOC $\Delta^{14}C$
331 values (Figure 2). The polarity-driven SPE method and its lower extraction efficiency for
332 dissolved organic nitrogen compared to organic carbon may be responsible for the difference
333 between total DOC and SPE-DOC $\Delta^{14}C$ values (Flerus et al., 2012). Another possible
334 explanation for this offset could be selective concentration of older humic materials that were
335 precipitated out of solution at pH 2 during the collection of the standards (a step that we use in
336 our SPE method). Our results suggest that SPE-DOC selectively isolates older DOC from the
337 riverine standards, and to a lesser extent for seawater samples.
338 Using a mass balance between the SPE-DOC that is recovered (43±6%) and total DOC,
339 we find the non-adsorbed DOC (57±5%) is more modern than their SPE-DOC counterpart by
340 67‰, 38‰, 9‰ and 17‰ for SR NOM I, SR NOM II, NBP and Station M, respectively
341 (Supplementary Figure 2). For freshwater systems, the non-adsorbed DOC $\Delta^{14}C$ value is
342 significantly different from the SPE-DOC $\Delta^{14}C$ value. For marine samples, the non-adsorbed
343 DOC $\Delta^{14}C$ value is within error to the total DOC and SPE-DOC $\Delta^{14}C$ values (Supplementary

Figure 2). While our sample set is limited, these results suggest that SPE-DOC $\Delta^{14}C$ results may be within error of the total DOC pool.

4.3 Comparison of SPE-BC, total BC and UDOC BC $\Delta^{14}C$ values and BPCA distributions

In contrast to SPE-DOC and bulk DOC, comparisons between SPE-BC and total BC of SR NOM I and II standards show BPCA distributions and $\Delta^{14}C$ values that are dissimilar to one another. This may indicate different sources, or differential cycling of BC within DOC. For SR NOM I and II, non-adsorbed BC had a more aromatically condensed structure (greater abundance of B6CAs) than that for total BC (Table 3). The BPCA relative abundances reveal that SPE-BC isolates are more aromatically condensed than BC from the total BC pool. Additionally, the SPE-BC $\Delta^{14}C$ value of SR NOM I is higher than that of total BC, while SR NOM II is lower than that of the total BC. This may be due to variations in the environmental conditions present during sample collection between 1999 and 2012, or by differential cycling between SPE-BC and total BC.

Ultrafiltration concentrates DOC based on size, whereas SPE chemically sorbs DOC based on polarity. We show that a more aromatically condensed BC structure (higher relative abundance of B6CAs) and higher $\Delta^{14}C$ values were found for the SPE-BC (Figure 4a) than for the UDOC (Ziolkowski and Druffel, 2010). Based on size-reactivity it was expected that the higher molecular weight (UDOC) fraction of BC would be younger than the age of SPE-BC, if BC followed the same size-reactivity relationships of DOC (see review by Benner and Amon, 2015). BC concentration has been found to correlate with DOC concentration (Jaffe et al., 2013) in environmental waters. This suggests that with a larger DOC sample pool (43%), total BC may not be as aged as previously thought, or that there is discreet cycling of BC within these DOC

367 fractions. Nonetheless, a larger sample set is needed to explain the relationship of the BC DOC
368 fractions.
369
370 4.3. SPE-DOC and BC cycling
371 Here, we investigate the different polarities of the SPE-DOC elutant fractions in the
372 context of understanding DOC composition and cycling within these pools. By comparing the
373 recovery of SPE-DOC in each of the polar and non-polar fractions, we found that the riverine SR
374 NOM I and II standards were exclusively polar with no significant differences in SPE-DOC
375 composition between the two collection periods (Figure 3, Table 2). Methanol SPE-DOC is
376 composed of younger (perhaps humic, and/or carbohydrate-like) materials.
377 In contrast, NBP and Station M seawater samples have higher proportions of SPE-DOC
378 eluting in the less polar fractions (Figure 3). Approximately 10% of oceanic SPE-DOC at
379 Station M eluted with non-polar solvents. This agrees with previous studies that showed
380 individual DOC fractions can have distinct compositions and low $\Delta^{14}C$ values in the ocean, such
381 as lipid-like compounds or acid insoluble fractions in DOC and particles (Loh et al., 2006; Wang
382 et al., 2006; Hwang and Druffel, 2003).
383 Total DOC $\Delta^{14}C$ values, BPCA relative abundances and BC $\Delta^{14}C$ values in SR NOM I
384 and II are dissimilar. Suwannee River NOM I and II represent different amounts of
385 anthropogenic influence. We observe similar BC concentrations and different $\Delta^{14}C$ values of the
386 BC in these river standards. Suwannee River NOM I BC has high $\Delta^{14}C$ values, perhaps
387 indicative of the extensive fires in the swamp in the mid-1950s (Green et al., 2015). Both DOC
388 and BC $\Delta^{14}C$ values were higher in 1999 (SR NOM I) than 2012 (SR NOM II) (Figure 2),
389 suggesting an older DOC and BC source contribution in SR NOM II. The more aromatically

condensed structure and lower BC $\Delta^{14}C$ value of SR NOM II likely suggests anthropogenic fossil fuel input, as the Suwannee River sampling site is no longer considered pristine (Green et al., 2015) (Figure 4a). Hydrophobic acid isolates from reverse osmosis of SR NOM collected in 2012 have a higher average molecular weight, and ^{13}C NMR studies revealed more aromatic functional groups than for SR NOM I (Kreller et al., 2015; Nwosu and Cook, 2014). This suggests that riverine BC is influenced by anthropogenic input. It cannot be assumed that all riverine BC enters the ocean with modern $\Delta^{14}C$ values, as preliminary work has suggested (Ziolkowski and Druffel, 2010).

Oceanic BC appears chemically distinct from the riverine samples we studied. Using the relative BPCA abundance as an indicator of BC aromaticity, we observe a smaller contribution of B3CAs in SR NOM I and II versus marine SPE-BC (Figure 4a). Our oceanic sample results also provide us with a glimpse of DOC-BC cycling at coastal and open ocean sites. Coastal NBP is the only sample with significant amounts of SPE-BC in all four solvent fractions (SPE-BC = 4±0.4 μM C). Given the high BC content, we believe this site is influenced by fossil fuels or local aged sources. Similarly, total suspended solids for a nearby river (~75 miles north, Santa Clara River, CA) had 44.3% BC/OC%, suggesting a large BC riverine flux from the Ventura Basin, with low $\Delta^{14}C$ values of -644±58‰ (Masiello and Druffel, 2001). This may explain the high BC content we observe in NBP (20±2%) samples. This coastal site was expected to have low BC $\Delta^{14}C$ values because of possible input from the urban Santa Ana River (greater abundance of B6CAs, much like SR NOM II) (Supplementary Figure 1).

Although the SPE-BC $\Delta^{14}C$ values are within error at NBP and Station M, the relative BPCA abundances may reveal reprocessing of the oceanic BC pool. We assume BC at Station M is representative of open ocean BC (with no riverine anthropogenic sources), while coastal BC

413 is influenced by anthropogenic riverine BC. The structure of BC at Station M has a greater
414 relative abundance of B3CAs than NBP (Figure 4a). This may indicate degradation processes
415 removing aromatic BPCAs with transport to the open ocean (e.g. photo-oxidation; Stubbins et al.,
416 2012). At Station M, we suggest SPE-BC persists 7,800±1,700 ^{14}C yrs in the open ocean. SPE-
417 BC is about 12,000 ^{14}C yrs younger than BC isolated from UDOC at Station M (20,100±3000
418 ^{14}C yrs; Ziolkowski and Druffel, 2010). However, more measurements are needed to constrain
419 the sources, cycling and ^{14}C age of BC in the global ocean, in particular the apparent differential
420 cycling between SPE-BC and UDOC.
421
422 **5. Summary and Implications**
423 We report a modified, low-blank SPE method to isolate DOC from fresh and marine
424 water samples. We report that SPE-DOC seawater isolate constitutes nearly half of the DOC
425 pool (43±6%). We present the first Δ^{14}C blank assessments of the SPE-DOC method from a
426 limited set of river standards and surface ocean water samples. In comparison to total DOC Δ^{14}C
427 values for these same samples, we found that SPE-DOC Δ^{14}C are 35 ±10‰ lower than total
428 DOC Δ^{14}C for freshwater samples. In contrast, marine SPE-DOC Δ^{14}C values were low, but
429 within error of total DOC Δ^{14}C values. We observe similar SPE-BC Δ^{14}C values in our coastal
430 and open ocean sites, but different BPCA relative abundances.
431 Further measurements are needed to determine BC Δ^{14}C and structure (using relative
432 BPCA distributions) to better understand the sources, sinks and cycling of BC in aquatic
433 environments. One limitation of these analyses was the sample size of non-polar SPE-DOC,
434 which prevented analysis of relative BPCA abundances and Δ^{14}C values of non-polar BC at our
435 open ocean site. The use of larger water samples will allow for non-polar BC to be evaluated

436 and placed into the context of total and SPE-DOC ^{14}C ages. Additional research seeking
437 chemically characterize SPE-DOC fractions at the molecular level (e.g nuclear magnetic
438 resonance and Fourier transform ion cyclotron resonance mass spectrometry, FT-ICRMS), which
439 will reveal compositional relationships between SPE-DOC and SPE-BC.
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